Continental inputs of C, N, P and Si species to the Ría de Vigo (NW Spain)

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Abstract

C, N, P and Si in dissolved, particulate, organic and inorganic forms, determined from 12 surveys in the river Oitabén–Verdugo during 2002, allowed quantification of the chemical composition, phase partitioning and fluxes of continental materials to the inner Ría de Vigo (NW Spain). Despite the large fluxes normalised to the drainage basin of the river Oitabén–Verdugo (280 mmol C m^{-2} y^{-1}, 56.5 mmol N m^{-2} y^{-1}, 1.35 mmol P m^{-2} y^{-1}, and 61.3 mmol Si m^{-2} y^{-1}), its reduced dimensions (350 km^2) yielded relatively low concentrations of these species. Organic C, N and P represented 62%, 43% and 48% of the total C, N and P fluxes, respectively. About 90% of the organic C and N and 60% of the organic P was in the dissolved form. The chemical composition of the organic materials was compatible with detrital organic matter derived from aquatic plants, phytoplankton and soil leaching but not with unprocessed terrestrial plants. Significant temporal changes were observed in the chemical composition, related to the seasonal cycle of the biological activity in stream waters and soils, as well as the chemical weathering reactions. Spatial differences were due to the contrasting dynamic regime and, likely, the origin of the materials.

Keywords: nutrients, organic matter, river fluxes, Ría de Vigo (NW Spain)

1. Introduction

Carbon and nutrient cycles in ocean margins are fuelled by the input of nutrient salts from the continents, the atmosphere, and the adjacent ocean. In the global coastal zone, 70% of the nitrogen input comes from the ocean, 22% from the continents and 8% from the atmosphere (Wollast, 1993). However, these percentages are very variable from site to site. Continental inputs could become dominant in large drainage basins dedicated to intensive agriculture and farming, where rivers play a major role in the transference of materials from land to sea and influence significantly the biogeochemical processes in coastal waters. Atmospheric inputs are specially relevant in highly industrialised coastal areas (Duce *et al.*, 1991). Finally, the open ocean is the main source of external nutrient salts in the coastal upwelling areas associated to ocean eastern boundary currents (Walsh, 1991).

In the case of the coastal upwelling system of the Iberian Peninsula (SW Europe), major rivers drain into the Portuguese coast; specially the polluted Douro (550 $m^3 s^{-1}$) and Tejo (450 $m^3 s^{-1}$) rivers in Porto (41ºN) and Lisbon (39ºN), respectively (Kempe *et al.*, 1991). In the northern boundary of this area (42ºN–43ºN), the Rías Baixas, four large (>2.5 km^3) coastal inlets, receive the continental input of a small drainage basin (6800 Km^2), with an average annual flow of 205 $m^3 s^{-1}$ (Álvarez–Salgado *et al.*, 2002). The main tributary to the Ría de Vigo, the southernmost of the Rías Baixas, is the river Oitabén–Verdugo, which is not significantly affected by industrial or sewage waste waters (Pérez *et al.*, 1992). The drainage basin of the river Oitabén–Verdugo has a total surface area of 350 km^2 and receives a rainfall of 2500 mm y^{-1} (Ríos *et al.*, 1992) that produces an average flow of 15 $m^3 s^{-1}$ (Nogueira *et al.*, 1997). This river drains into San Simón bay, the innermost part of the Ría de Vigo, a basin of ~20 km^2, 30% of which becomes dry at low tide.

Most of the scientific effort in the Ría de Vigo has been focused on the effect of the intermittent entry of nutrient salts from the adjacent ocean during the recurrent upwelling episodes of the spring and summer (e.g. Prego, 1994; Gilcoto *et al.*, 2001; Gago *et al.*, 2003). Despite continental inputs being low at this time of the year (<10 m^3 s^{-1}; Nogueira *et al.*, 1997), ~10% of the inorganic nitrogen consumed in the rías comes from the drainage basin (Álvarez–Salgado *et al.*, 1996). The contribution increases during the autumn and winter, when higher river flows are recorded (>25 m^3 s^{-1}) and frequent downwelling episodes introduce the nutrient–poor surface waters of the adjacent shelf into the ría (Álvarez–Salgado *et al.*, 2002).

Nutrient dynamics in the rivers draining into the Rías Baixas remains poorly understood, and little attention has been paid to the quantification of the transport of continental materials and its seasonal variation. The aim of this work is to ameliorate this lack of knowledge about the continental waters draining into the inner Ría de Vigo through a study of nutrient concentrations, partitioning between dissolved/particulate and organic/inorganic phases, fluxes and their respective temporal variation during a seasonal cycle.

2. Material and methods

2.1. Sampling programme

Water samples were collected once a week, during 3 consecutive weeks, in February, April, July and September 2002. Three sampling points were visited (Figure 1): 1) the bridge of Arcade, at the mouth of the river Oitabén–Verdugo (salinity > 15); 2) the bridge of Soutomaior, in the upstream limit of the FSI (salinity <3); and 3) the Eiras reservoir, at the higher course of the river Oitabén (salinity <0.03).

Samples were collected at ~1 m depth with a PVC Niskin bottle. The Soutomaior bridge was visited during the low tide, to ensure that salinity was <3. Water for the chemical analyses was processed in the laboratory within a few hours of collection. Salinity, total alkalinity/total inorganic carbon, and nutrient samples were collected on dedicated flasks. Water for the other chemical variables was collected on acid cleaned amber glass flasks.

2.2. *Analytical methods*

Salinity (S). Samples were collected in glass bottles and determined from conductivity measurements using a Beckman salinometer with a precision of ±0.01 (UNESCO, 1985).

*Total alkalinity (*TA*) and total inorganic carbon (*C_T*).* Samples were collected in 500 ml all–glass flasks and poisoned with Hg_2Cl_2. A combined glass electrode was used to determine pH and TA was determined by potentiometric titration with HCl at a final pH of 4.44 (Pérez and Fraga, 1987). This method has a precision of ±1.4 μeq l^{-1}. Total inorganic carbon (C_T) was calculated from pH and TA with the Lueker *et al.* (2000) carbonic and boric acid dissociation constants. The precision of this calculation is ±3 μmol C l^{-1}.

*Nutrient salts***.** Samples were collected in 50 ml polyethylene bottles; they were frozen until analysis using standard segmented flow analysis (SFA) procedures. The precision is ±0.02 μmol l^{-1} for NO_2^- and HPO_4^{2-}, ±0.1 μmol l^{-1} for NO_3^- and ±0.05 μmol l^{-1} for NH_4^+ and $Si(OH)_4$.

Dissolved organic carbon (DOC) and *nitrogen* (DON). Samples were filtered through precombusted GF/F filters in an acid–cleaned glass filtration system, under low N_2–flow pressure. The filtrate was collected in 10–ml precombusted glass ampoules. After acidification to pH < 2, the ampoules were heat–sealed and stored at 4ºC until analysis. They were measured with a nitrogen–specific Antek 7020 nitric oxide chemiluminescence detector coupled in series with the carbon–specific Infra–red Gas Analyser of a Shimadzu TOC–5000 organic carbon analyzer, as described in Álvarez–Salgado and Miller (1998) with a precision of ±0.7 μmol C l^{-1} and ±0.2 μmol N l^{-1}.

*Dissolved organic phosphorus (*DOP*).* The filtrate was collected in 50 ml polyethylene containers and frozen until analysis. It was measured with the SFA system for phosphate, after oxidation with $Na_2S_2O_8$/borax and UV radiation (Armstrong *et al.*, 1966). Only the organic mono–phosphoric esters are analysed because poly–phosphates are resistant to this oxidation procedure. The precision of the method is ±0.04 μmol P l^{-1}.

Dissolved mono– and polysaccharides (MCho and PCho). Sampling and storage was identical than for DOC/DON and DOP. MCho and PCho were determined by the oxidation of the free reduced sugars with 2, 4, 6–tripyridyl–s–triazine (TPTZ) followed by spectrophotometric analysis at 595 nm (Nieto–Cid *et al.*, 2004). The precision is ±0.6 μmol C l^{-1} for MCho and ±0.7 μmol C l^{-1} for TCho.

Particulate organic carbon and nitrogen (POC and PON). They were collected from 0.5–1.5 l of water on precombusted 25–mm ø Whatman GF/F filters under low–vacuum. Filters were dried overnight and frozen before analysis. Measurements of POC and PON were carried out with a Perkin Elmer 2400 CHN analyzer. The precision of the method is ±0.3 μmol C l^{-1} and ±0.1 μmol N l^{-1}.

Particulate organic phosphorus (POP). It was collected from 200 ml of water on precombusted 25–mm ø Whatman GF/F filters under low–vacuum. It was determined by H_2SO_4/$HClO_4$ digestion at 220ºC of the particulate material. After neutralisation with ammonia, the produced phosphoric acid was analysed by SFA. The precision for the entire analysis is ±0.02 μmol P l^{-1}.

Particulate carbohydrates **(**p–Cho). They were collected from 200 ml of water on precombusted 25–mm ø Whatman GF/F filters under low–vacuum. The analyses were carried out by the anthrone method (Ríos *et al.*, 1998), with a precision of ±0.1 μmol C l^{-1}.

2.3. Continental runoff

Daily flows from the Eiras reservoir were provided by the company in charge of the management of urban waters (SERAGUAS S.A.). They represented 42±16% of the total flow of the River Oitabén–Verdugo during the study year. The natural component of the flow per unit area (R/A) was calculated with the empirical formula of Ríos *et al.* (1992), from the precipitation (P) in the drainage basin:

$$\frac{\mathrm{R}}{\mathrm{A}} = \frac{1 - 0.75}{0.75 - 0.75^{31}} \cdot \sum_{n=1}^{30} \mathrm{P(n)} \cdot \mathrm{k}^{\mathrm{n}} \qquad (1)$$

This equation accounts for the influence of daily precipitation during the 30 days before the study day.

3. Results

3.1. Inorganic chemical composition of continental waters

The average chemical composition of continental waters, at the seasonal and annual time scales, is presented in Table 1 for the high course of the River Oitabén at the Eiras reservoir (average salinity, 0.02±0.01) and the upstream limit of the FSI of the River Oitabén–Verdugo at the Soutomaior bridge (average salinity, 1.3±1.3).

The pH of continental waters at the Eiras reservoir ranged from 6.6 to 7.8. pH was significantly higher ($p < 0.01$) than in the Soutomaior bridge, where it varied between 6.3 and 6.8 (Table 1). TA and C_T exhibited a marked seasonal trend, increasing from winter minimum to autumn maximum values at the Eiras reservoir. The same trend should be observed at the Soutomaior bridge, but the salinity increase at the upstream limit of the FSI from 0.02 in winter to 3.3 in autumn masked this effect with the mixing of the TA– and C_T–poor river water end member and the TA– and C_T–rich sea water end member. Average annual TA and C_T at the Soutomaior bridge extrapolated to salinity zero were 25±8 μeq l^{-1}

and 42±7 µmol C l^{-1} ($r^2 > 0.97$, n = 15, $p < 0.001$). Although other variables, such as DOM, POM, HPO_4^{2-} and $Si(OH)_4$ also correlated with salinity ($r^2 < 0.60$), the seasonal changes in their concentrations cannot be ascribed to the simple mixing of fresh and sea water: the observed levels are much higher than the characteristic concentrations of these variables for S = 35 in the Ría de Vigo (Doval et al., 1997).

For the case of the inorganic nitrogen (N_T) species, NH_4^+ , NO_2^- and NO_3^- levels at the Soutomaior bridge were significantly higher than at the Eiras reservoir ($p < 0.01$). Nitrate was the prevailing N_T form: it represented >80% of N_T in both sites, except during the autumn at the Eiras reservoir, when ammonium was 30% of N_T. NO_3^- at the Eiras reservoir decreased ($p < 0.001$) and NH_4^+ in the Soutomaior bridge ($p < 0.001$) increased significantly from winter to autumn (Table 1).

As for N_T, HPO_4^{2-} levels were significantly higher at the Soutomaior bridge than at the Eiras reservoir ($p < 0.05$). Whereas HPO_4^{2-} was constant through the annual cycle at the Eiras reservoir ($p > 0.28$), a significant increase was observed at the Soutomaior bridge from winter to autumn ($p < 0.05$). Regarding dissolved silica (SiO_4H_4), concentrations were also significantly higher, about 4–fold, at the Soutomaior bridge than at the Eiras reservoir ($p < 0.05$), specially during the summer and autumn (Table 1).

3.2. Organic chemical composition of continental waters

Average DOC levels were non significantly different between the Soutomaior bridge and the Eiras reservoir ($p > 0.44$). On the contrary, DON and DOP levels were significantly higher at the Soutomaior bridge ($p < 0.001$). At this site, DOC and DON increased from a winter minimum to an autumn maximum, whereas DOP was relatively constant (Table 1). Annual average C/N/P molar ratios ranged from 345/50/1 at the Soutomaior bridge to 825/70/1 at the Eiras reservoir.

Whereas MCho were constant through the study period (average, 22–23 µmol C l^{-1}; $p > 0.65$), marked changes were observed in PCho, varying from a winter minimum to a summer maximum at both sites (Table 1). PCho were significantly higher at the Eiras reservoir (average, 21 µmol C l^{-1}) than at the Soutomaior bridge (average, 8 µmol C l^{-1}; $p < 0.001$). Carbohydrates were a major component of the DOC pool: they represented from 30% in winter to 60% in summer (average 50%) of the DOC at the Eiras reservoir and from 30% in winter to 50% in summer (average 40%) at the Soutomaior bridge.

POC, PON and POP at the Eiras reservoir were characterised by a winter minimum, slightly higher concentrations in spring and summer, and a remarkable maximum in autumn (Table 1). POC and PON concentrations were significantly higher at the Eiras reservoir than at the Soutomaior bridge ($p < 0.005$), about 3–4 fold, and exhibited also a seasonal trend with a winter minimum and a summer/autumn maximum. Average C/N/P molar ratios of POM ranged from 97/14/1 at the Soutomaior bridge to 272/31/1 at the Eiras reservoir.

The seasonal pattern of p–Cho was similar to POC, with an increase from winter to autumn, either at the Eiras reservoir or the Soutomaior bridge (Table 1). Average concentrations were 6–fold in Eiras than in Soutomaior. p–Cho represented 17±4% in Soutomaior and 28±6% in Eiras of the POC (mol C/mol C).

Assuming that the spatial and temporal changes in the C/N/P composition of POM are due to variations in the proportions of the four major groups of biomolecules (carbohydrates, lipids, proteins and phosphorus compounds) rather than variations in the molecular formula of each group, it is possible to estimate these proportions as follows. Fraga *et al.* (1998) reviewed the average composition of carbohydrates (Cho, $C_6H_{10}O_5$), lipids (Lip, $C_{53}H_{89}O_6$), proteins (Prt, $C_{147}H_{227}O_{46}N_{40}S$) and phosphorus compounds (Pho, $C_{45}H_{76}O_{31}N_{12}P_5$). From the chemical formula of these biomolecules, the following set of five linear equations can be written for POM:

$$C = 147 \times Prt + 6 \times Cho + 53 \times Lip + 45 \times Pho \quad (2)$$

$$H = 227 \times Prt + 10 \times Cho + 89 \times Lip + 76 \times Pho \quad (3)$$

$$O = 46 \times Prt + 5 \times Cho + 6 \times Lip + 31 \times Pho \quad (4)$$

$$N = 40 \times Prt + 12 \times Pho \quad (5)$$

$$P = 5 \times Pho \quad (6)$$

Since particulate C, N, P and Cho were measured, the system can be solved to obtain the average chemical formula, and the proportions of the different biomolecules for each particular sample. The five unknowns are H, O, Prt, Lip and Pho.

Figure 2 shows a ternary plot of the contribution of proteins+phosphorus compounds (N/P compounds), carbohydrates and lipids to the particulate organic matter (mol C/mol C) at the Eiras reservoir, the Soutomaior bridge and the Arcade bridge. A significant downstream increase of N/P rich compounds and a decrease of carbohydrates were observed ($p < 0.001$). The contribution of lipids, the most recalcitrant material, was not significantly different from site to site ($p > 0.43$).

3.3. *Annual fluxes of continental materials*

The average flow of the river Oitabén–Verdugo into San Simón bay during 2002 was 17 $m^3 \; s^{-1}$. Maximum discharges (150 $m^3 \; s^{-1}$) were observed in December, whereas minimum values (3 $m^3 \; s^{-1}$) were found in August and September. Table 1 summarises the net fluxes of the different C, N, P and Si species during the study year from the concentrations measured at the Soutomaior bridge. The total carbon flux to San Simón bay, 1178 Tn C y^{-1}, was dominated by DOC (53%), and followed by C_T (39%). The Cho flux, 247 Tn C y^{-1}, represented 34% and 21% of the organic and total C fluxes, respectively. The most abundant form was the labile dissolved monossacharides: 25% of the organic C flux. The total N flux, 277 Tn of N

y^{-1}, was dominated by nitrate (49%) and DON (37%). Ammonium and PON, main reservoirs of the labile amine groups, represented together only 13% of the total N flux. P and Si inputs were about 15 Tn P y^{-1} and 600 Tn Si y^{-1}. For the case of P, half of the material was in organic forms (DOP and POP).

3.4. Behaviour during estuarine mixing

Salinity at the Arcade bridge, at the mouth of the river Oitabén–Verdugo, ranged from 15 to 32 throughout the study period. The linear correlation coefficient between salinity and the different C, N, P and Si species can be used as an index of the conservativeness of these species during estuarine mixing. Since data taken at different times of the year are analysed together, it should be kept in mind that departure from the conservative behaviour could be due to either the reactivity of the chemical species during estuarine mixing or the observed seasonal changes in the freshwater and sea water end members that mix in the FSI (Officer and Lynch, 1981; Loder and Reichard, 1981).

Some of the species exhibited a conservative behaviour despite the seasonal changes in the freshwater end member. This is the case of TA ($r^2 = 0.998$, n = 42, $p < 0.001$) and C_T ($r^2 = 0.994$, n = 42, $p < 0.001$), likely because of the 2–orders–of–magnitude difference between the concentrations of the freshwater and seawater end members. The samples from the three sites were considered in these linear regression analyses. The origin intercepts of the regression equations, 39±7 μeq l^{-1} for TA and 62±12 μmol C l^{-1} for C_T, can be used as an average composition of the river end member.

Silicate also behaves conservatively at the Arcade bridge ($r^2 = 0.91$; n= 12; $p < 0.001$) with an origin intercept of 65±2 μmol Si l^{-1}. This behaviour is specially remarkable considering that silicate concentrations at the Soutomaior bridge approached the origin intercept value only during the summer and autumn, with concentrations <20 µmol Si l^{-1}) during the winter and spring (**Table 1**).

Other dissolved species correlated significantly with salinity (p < 0.01), but this variable explained a lower proportion of the total variability. This was the case of NO_3^- (r^2 = 0.85, origin intercept = 15.4±0.7 µmol N l^{-1}), MCho (r^2 = 0.63, origin intercept = 24±1 µmol C l^{-1}), HPO_4^{2-} (r^2 = 0.58, origin intercept = 0.17±0.06 µmol C l^{-1}), DOP (r^2 = 0.50, origin intercept = 0.21±0.02 µmol P l^{-1}) and DOC (r^2 = 0.36, origin intercept= 83±6 µmol C l^{-1}). Positive slopes (higher concentrations in the river end member) were computed for NO_3^- and MCho, whereas they were negative (higher concentrations in the seawater end member) for HPO_4^{2-}, DOP and DOC.

4. Discussion

4.1. *C, N, P and Si composition and partitioning in an unpolluted western European littoral river stream*

The extension and the topography of the drainage basin, the rainfall regime, together with the nature of the soil (occurrence of highly soluble or easily weathered minerals) and the different land uses (forest, agriculture, industry, urban settlements, occurrence of peat bogs, wetlands and marshes), determines the inorganic and organic nutrient loads of a river stream (Meybeck and Helmer, 1989; Esser and Kohlmaier, 1991; Mulholland, 1997). For the rivers draining into the Galician Rías Baixas, the drainage basins receive abundant rain (2500 mm y^{-1}), which produces a large average flow per unit area of 37 l s^{-1} km^{-2} (Nogueira *et al.*, 1997). However, the fragmentation in several small drainage basins (<500 Km^2) leads to reduced individual river flows. The average annual flow of the river Oitabén–Verdugo is 15 m^3 s^{-1} , ranging from >25 m^3 s^{-1} from October to January and then decreases to <5 m^3 s^{-1} in August (Nogueira *et al.*, 1997). These are common characteristics of west European littoral systems, together with the impermeability of soils and the distance from industrial and urban outfalls (Treguer and Queguiner, 1989). A remarkable difference is the prevailing use of the drainage basin by intensive agriculture in west European littoral systems compared with the more pristine nature of the river Oitabén–Verdugo.

Chemical weathering of surficial rocks and leaching of organic soils are the main terrestrial sources of inorganic and organic nutrients in unpolluted rivers . A significant flushing effect, *i.e.* a positive relationship between river flows and nutrient loads, is commonly observed in these systems (Esser and Kohlmaier, 1991; Spitzy and Leenheer, 1991), suggesting that larger streams have generally higher nutrient concentrations than smaller streams (Mullholland, 1997). Although the nutrient specific fluxes normalised to the drainage basin of the river Oitabén–Verdugo are high (32 mmol N m^{-2} y^{-1}, 0.70 mmol P m^{-2} y^{-1} and 61 mmol Si m^{-2} y^{-1}) compared with other unpolluted rivers (Guo *et al.*, 2004), the relatively low flow of this river is likely the main reason behind their reduced inorganic and organic nutrient concentrations.

Inorganic N and P in the River Oitabén–Verdugo, comparable with the average values proposed by Meybeck (1982) for unpolluted rivers, contrasted with the one–order–of–magnitude higher concentrations recorded in the polluted 23 rivers draining into the adjacent Cantabrian sea, with comparable drainage basins (average, 800 km^2) and river flow regimes (average, 28 l s^{-1} km^{-2}): nitrate, 120±175 µmol N l^{-1}; nitrite, 4.7±6.5, µmol N l^{-1}; ammonium, 15±27 µmol N l^{-1}; and phosphate, 13±19 µmol P l^{-1} (Prego and Vergara, 1998). Nutrient levels in the river Oitabén–Verdugo are also lower than the average concentrations proposed by Prego *et al.* (1999) for the rivers draining into the Galician rías during the dry season: 50–60 µmol N l^{-1} nitrate; 0.1–0.2 µmol N l^{-1} nitrite; 2–9 µmol N l^{-1} ammonium; and 0.6–0.7 µmol P l^{-1} phosphate.

On basis of the inorganic N (ammonium, nitrite and nitrate) and phosphate measurements in the Oitabén–Verdugo river basin, an average N/P molar ratio of 63±44 was obtained, which is significantly higher than the Redfield ratio of 16 for aquatic plants and phytoplankton (Anderson 1995; Fraga *et al.,* 1998). It indicates that the river Oitabén–Verdugo is P–limited, as most continental aquatic ecosystems (Turner *et al.*, 2003).

Inorganic C and silicate in rivers derive mainly from the weathering of carbonate and silicate minerals. The concentrations of both species in the river Oitabén–Verdugo are ~1/3 of the average values obtained by Meybeck and Helmer (1989) in freshwater streams draining granite rocks: 130 μmol Si l^{-1} and 150 μmol C l^{-1}, respectively. However, the silicate specific flux normalised to the drainage basin of the river Oitabén–Verdugo, 60 mmol m^{-2} y^{-1}, is about twice the expected value according to the general trend of increase in silicate specific flux with decreasing latitude in Northern hemisphere major rivers (Guo *et al.*, 2004). This seems to reflect the universal trend to higher organic activity in soils, as well as faster rates of the chemical weathering reactions, in warmer climate rivers.

DOC ranges from <50 μmol C l^{-1} in small rivers in Artic and alpine streams to >3000 μmol C l^{-1} in some tropical or polluted rivers and rivers draining into swamps and wetlands (Sedell and Dahm, 1990; Spitzy and Leenheer, 1991; Mulholland, 1997). A global average of ~400 μmol C l^{-1}, equivalent to a transport of 1900 kg C km^{-2} y^{-1}, remains a good estimate (Sedell and Dahm, 1990). Therefore, although the transport of 1800 kg C km^{-2} y^{-1} obtained in the river Oitabén-Verdugo is similar to the World average, the reduced drainage basin produces an average concentration of only 80±20 μmol C l^{-1}, characteristic again of a small unpolluted stream. This is also the case of DON and DOP. The C/N/P stoichiometry of DOM at the Soutomaior bridge (345/50/1) and the Eiras reservoir (825/70/1) are also within the ranges observed in unpolluted rivers: 360–7800/30–170/1 (Meybeck, 1982).

Dissolved carbohydrates use to be <25% of the DOC in river streams (Spitzy and Leenheer, 1991; Murrell and Hollibaugh, 2000). In the river Oitabén-Verdugo they represent from 30 to 60% of the total DOC. Considering these high carbohydrate proportions and the C/N ratio of the bulk DOM, the C/N molar ratios of the DOM fraction that is not carbohydrates resulted to be as low as 4.3±0.6 at the Soutomaior bridge and 5.8±2.3 at the Eiras reservoir. These C/N ratios correspond to a N–rich very labile material. In addition, most of the dissolved carbohydrates at the Soutomaior bridge (>70%) are the labile monossacharides.

Concentrations of POC, PON and POP were one order of magnitude lower than the average for unpolluted rivers: 400 µmol C l^{-1}, 40 µmol N l^{-1} and 6.7 µmol P l^{-1} (Meybeck, 1982). As for the case of DOM, the C/N/P ratios of POM at the Soutomaior bridge (97/14/1) and the Eiras reservoir (272/31/1) are also within the ranges observed in unpolluted rivers (Meybeck, 1982).

Finally, the average DOC/(DOC+POC) ratio of the river Oitabén–Verdugo is 0.8±0.1, which is close to the upper limit of the range reported by Meybeck (1982) for the world rivers: between 0.1 and 0.9, with an average of 0.6.

4.2. *Seasonal and spatial differences in C, N, P and Si composition and transport of river streams*

Small streams are usually more variable in inorganic and organic nutrient concentrations than larger streams and rivers (Sedell and Dahm, 1990). The Oitabén–Verdugo, a small river according to the classification of Meybeck *et al.* (1992), showed a marked seasonal variation in the concentration of most chemical species at the upstream limit of the FSI. In general, organic C, N, and P, either in suspended or dissolved forms, increased significantly from a winter minimum to a summer/autumn maximum. This was the case of some inorganic forms, such as ammonium and phosphate, generated also by leaching of organic soils (Meybeck *et al.*, 1992). Silicate concentration in the river stream also increased from winter to autumn. The common trend observed in all these chemical species reflects the seasonal cycle of the biological activity in stream waters and soils (Sedell and Dahm, 1990), as well as the chemical weathering reactions, which are directly related to the seasonal cycle of ambient light and temperature.

The concentration of inorganic nutrients was significantly lower at the Eiras reservoir than at the Soutomaior bridge, specially silicate, and the opposite was observed for particulate organic matter. This spatial pattern was probably the result of the intensified biogeochemical activity at the reservoir due to increased water residence time, which allow more phytoplankton production to occur and sediments to settle, followed by C, N, P and Si burial (Turner *et al.*, 2003).

There are also significant differences in the C/N/P stoichiometry of the particulate and dissolved organic matter at the Eiras reservoir and the Soutomaior bridge. In general, the organic material at Eiras presents a larger C/N/P ratio than at Soutomaior, a clear indication of the higher lability of the latter. In fact, the average C/N/P molar ratio of POM at the Soutomaior bridge (97/14/1) was close to the Refield ratio (106/16/1), typical of detrital organic matter derived from aquatic plants and phytoplankton (Anderson, 1995; Fraga *et al.*, 1998). On the other hand, the C/N/P ratio at the Eiras reservoir (272/31/1), was away from the Redfield ratio as a result of a marked increase in the proportion of particulate carbohydrates (58% of enrichment as compared with Soutomaior) at the expenses of proteins and phosphorus compounds (20% loss). This composition is typical of either N–limited aquatic plants and phytoplankton (Fraga *et al.*, 1998) or from soil leaching (Wafar et al., 1989). Since no nitrogen limitation was observed through the study period (N_T > 4 µmol N l^{-1}), soil leaching is the more likely explanation, as suggested by Wafar *et al.* (1989) in the Morlaix River (Brittany, France), where a 350/33/1 molar ratio was obtained. Unprocessed terrestrial plants, with characteristic C:N ratios ranging up to or exceeding 1000 and C:P ratios ranging up to or exceeding 800 (Likens *et al.*, 1981), are unlikely to be a relevant source for particulate material.

The proportion of carbohydrates in DOM was also larger at the Eiras reservoir (average, 50% of the DOC) than at the Soutomaior bridge (average, 37% of the DOC), and the difference was due to an excess concentration of polysaccharides.

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Table 1. Chemical composition (average concentration ± SD) at the Eiras reservoir (higher course) and the Soutomaior bridge (upstream limit of the FSI) and annual fluxes (Tn y^{-1}) of C, N, P and Si species discharged by the River Oitabén–Verdugo in San Simón bay during year 2002.

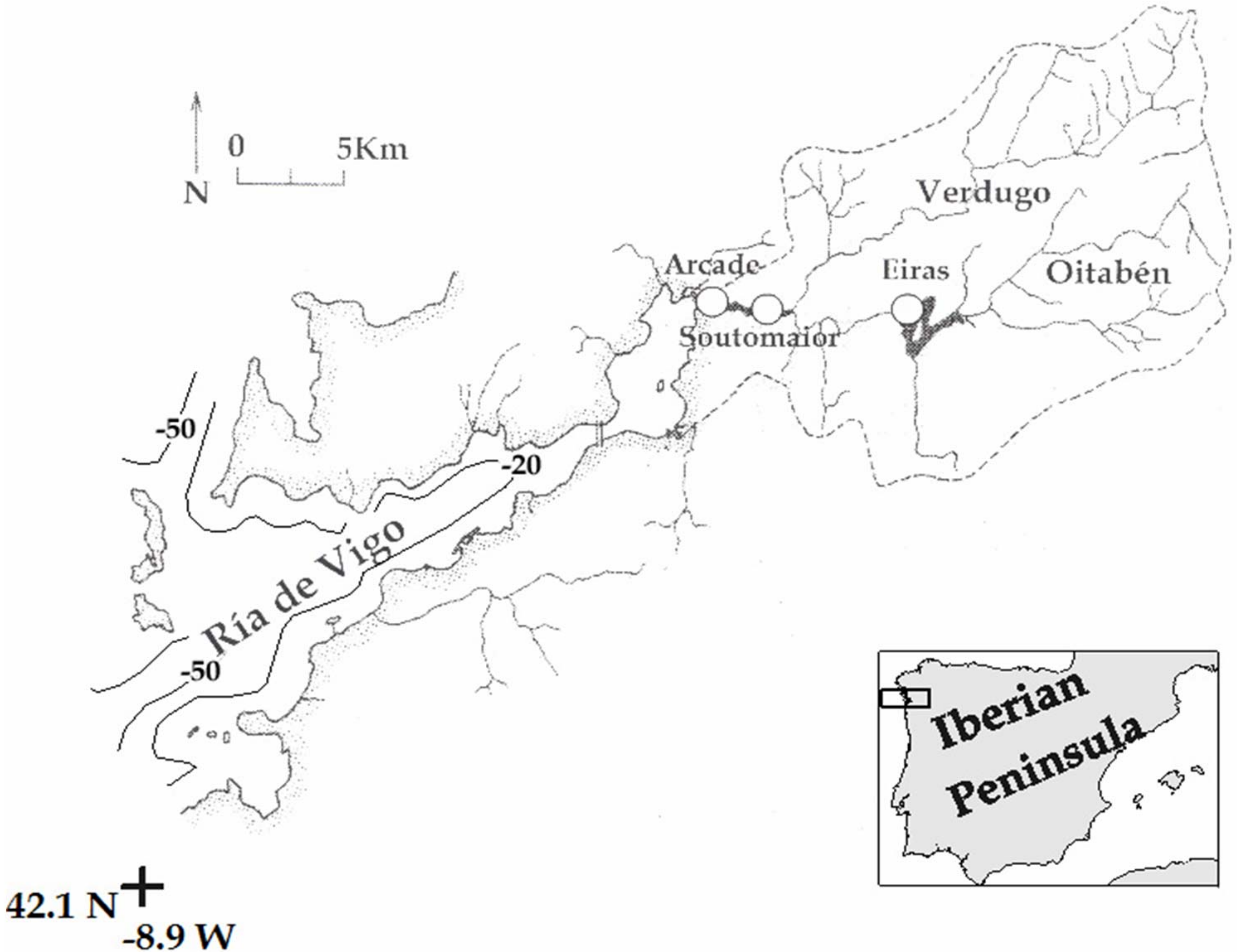
Property	Concentration (μmol l^{-1})										Annual Flux (Tn y^{-1})	
	Eiras reservoir					Soutomaior bridge						
	Winter	Spring	Summer	Autumn	Year	Winter	Spring	Summer	Autumn	Year		
S	0.02±0.01	0.02±0.01	0.02±0.01	0.02±0.01	0.02±0.01	0.02±0.01	0.14±0.06	2.02±0.98	3.34±0.35	1.26±1.34		
pH	7.23±0.59	6.62±0.70	7.13±0.51	7.76±0.56	7.17±0.63	6.70±0.13	6.27±0.05	6.75±0.17	6.91±0.12	6.62±0.26		
TA	7.0±2.5	15.7±3.2	40.1±4.6	42.1±4.6	30.6±14.9	26.7±5.7	35.9±7.6	194.4±81.0	330.9±31.4	25±8*		
C_T	7.3±1.5	25.1±11.6	45.5±6.6	41.5±7.6	34.8±15.7	33.3±4.9	61.5±9.8	236. 2±89.9	375.9±34.9	42±7*	453	39% of C
DOC	87±3	75±2	89±10	104±7	89±12	59±1	66±3	98±16	102±7	82±21	629	53% of C
POC	28±5	39±21	43±7	80±48	49±31	6.5±0.3	10.1±0.5	19.1±3.5	12.8±1.4	12.6±5.5	97	8% of C
MCho	26.8±1.5	24.5±2.6	20.9±0.7	23.0±0.5	23.5±2.5	17.8±0.4	23.9±1.9	24.0±0.3	23.6±0.9	22.5±2.9	175	71% of CH
PCho	2.7±1.0	22.7±15.9	24.5±16.3	25.8±5.4	21.3±14.5	2.0±0.1	9.0±9.5	10.2±7.6	8.7±5.7	8.2±7.1	55	22% of CH
p–Cho	5.6±0.6	12.2±9.8	12.2±1.9	21.3±15.2	13.3±9.5	1.2±0.1	1.7±0.6	3.0±0.9	2.6±0.5	2.1±1.0	17	7% of CH
NO_3^-	13.7±0.1	9.0±0.6	3.7±.1.6	2.6±0.1	6.0±4.2	17.6±0.2	12.7±0.8	15.1±.2.0	14.1±1.0	14.8±2.2	136.1	49% of N
NO_2^-	0.06±0.02	0.10±0.02	0.10±0.03	0.15±0.08	0.11±0.04	0.11±0.01	0.21±0.18	0.16±0.03	0.2±0.08	0.17±0.09	1.61	0.6% of N
NH_4^+	0.29±0.01	0.57±0.13	0.48±0.13	1.18±0.19	0.62±0.34	0.82±0.06	0.93±0.19	2.79±0.99	3.45±0.41	1.98±1.24	20.2	7% of N
DON	5.4±0.1	8.5±0.8	6.9±0.6	9.2±0.2	7.7±1.5	8.4±3.2	10.3±1.0	13.8±2.2	14.4±2.1	11.9±3.0	103.3	37% of N
PON	3.9±0.2	4.6±2.1	4.0±0.2	9.3±5.1	5.6±3.4	0.8±0.1	1.2±0.5	2.9±0.9	2.3±0.5	1.8±1.1	15.6	6% of N
HPO_4^{2-}	0.11±0.03	0.19±0.17	0.15±0.06	0.14±0.03	0.15±0.08	0.13±0.01	0.25±0.05	0.31±0.08	0.45±0.05	0.27±0.11	7.89	52% of P
DOP	0.16±0.04	0.07±0.04	0.11±0.03	0.15±0.06	0.12±0.05	0.18±0.02	0.22±0.02	0.28±0.10	0.21±0.05	0.24±0.08	4.23	28% of P
POP	0.08±0.02	0.14±0.09	0.11±0.04	0.36±0.23	0.17±0.15	0.06±0.01	0.07±0.02	0.19±0.05	0.20±0.02	0.13±0.07	2.99	20% of P
$Si(OH)_4$	1.9±0.1	4.1±0.9	10.3±6.8	8.6±1.6	7.4±5.5	12.2±9.8	4.7±1.1	51.7±.16.4	65.5±9.1	28.8±27.1	601	

*Annual average C_T and TA in the Soutomaior bridge were calculated extrapolating to salinity zero (r^2> 0.97, n = 15, p <0.001).

Figure captions

Fig. 1. Chart of the survey area, showing the three sampling sites in the Oitabén–Verdugo River (Ría de Vigo, NW Spain): the Eiras reservoir (higher course of the river), the Soutomaior Bridge (upstream limit of the fresh water–seawater interface) and the Arcade Bridge (upstream limit of the fresh water–seawater interface). Dashed line, boundaries of the drainage basin to the Ría de Vigo.

Fig. 2. Ternary plot of the contribution of N/P compounds, carbohydrates and lipids to the particulate organic matter pool (in mol C/mol C) for the three sampling sites in the Oitabén–Verdugo river.


N
0
5Km
Verdugo
Arcade
Eiras
Oitabén
Soutomaior
-50
-20
Ría de Vigo
-50
Iberian
Peninsula
42.1 N
-8.9 W

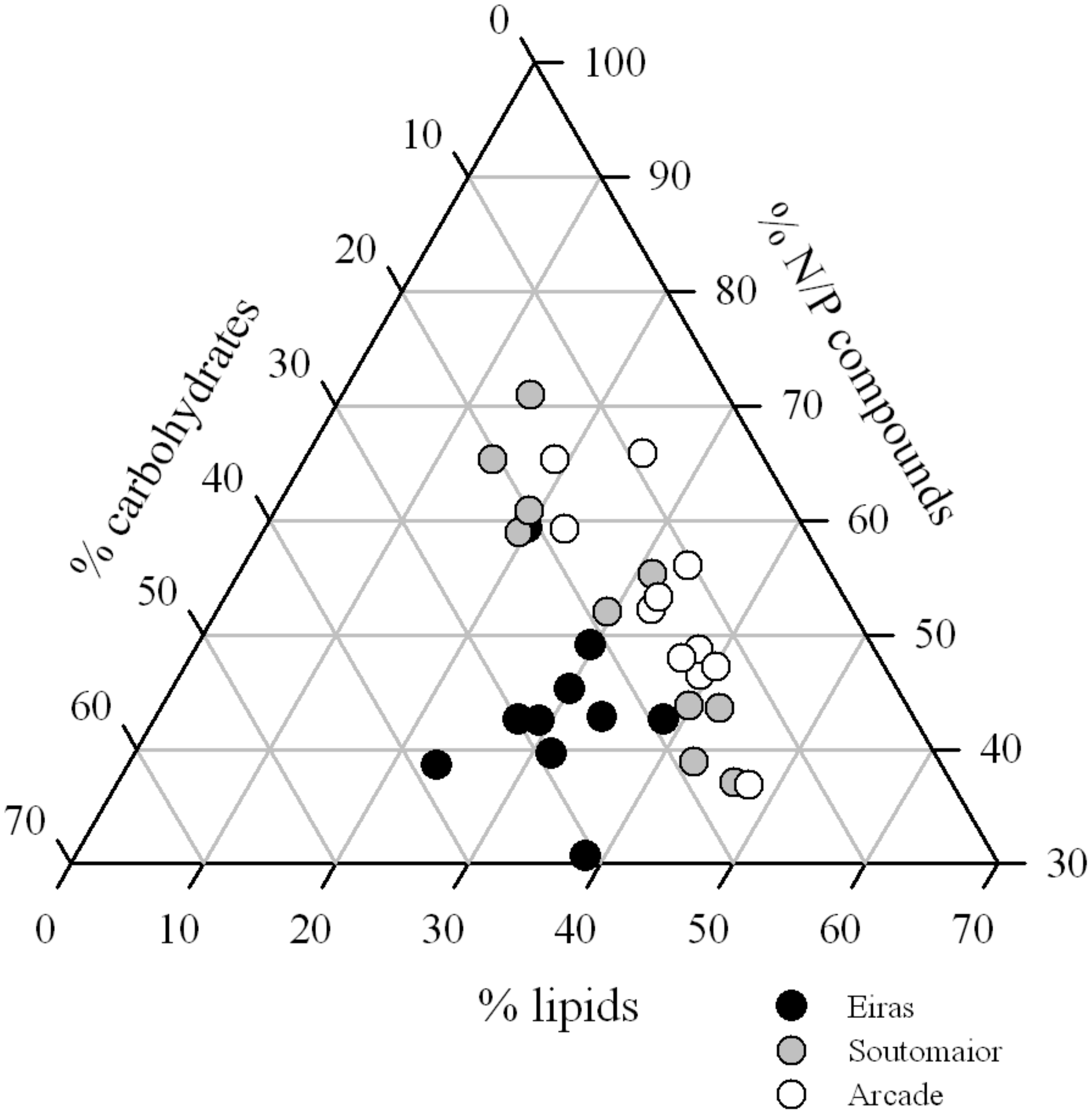


Figure 2, Gago et al.